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A WIDE RANGE WAVELENGTH MODULATION SPECTROMETER*

Ricardo Zucca† and Y. R. Shen‡

Department of Physics
University of California
Berkeley, California 94720

and

IMRD, Lawrence Berkeley Laboratory
Berkeley, California 94720

Abstract

A wavelength-modulation spectrometer with a spectral range of 2000-8000Å has been constructed. The system measures simultaneously the derivative spectrum and the conventional spectrum. The derivative spectrum has a sensitivity of $\Delta R/R \sim 10^{-5}$ and is completely free of background trouble. With proper changes in the optical components, the spectral range of the spectrometer can be extended further into the infrared and into the UV.

Technical Information Division
University of California
Lawrence Berkeley Laboratory
Berkeley, California 94720

I. INTRODUCTION

The advantages of derivative spectroscopy over conventional spectroscopy have long been exploited in EPR and NMR work.[1] Although theoretically derivative spectroscopy can not have better resolution than conventional spectroscopy in the zero noise limit, it does make spectral structures more apparent. That two closely overlapping peaks can be easily resolved in the derivative spectrum is a well-known example.[2] Small structures superimposed on a broad background can also be more readily detected in a derivative spectrum. The latter situation is fairly common in the optical spectra of solids.[3]

Optical derivative spectroscopy came into bloom only recently.[4] Several different modulation schemes were introduced. In most cases, the optical spectrum of the sample is modulated by an external ac perturbation, such as electric field,[5] pressure,[6] temperature,[7] light intensity,[8] etc., on the sample. The modulation spectrum so obtained depends intimately on how the property of the sample is affected by the external perturbation, and such knowledge is often limited. This is in contrast with the wavelength-modulation scheme, in which the wavelength of light is modulated, but no external ac perturbation is applied to the sample. In this latter case, a plain derivative spectrum is obtained.

The first optical wavelength modulation spectrometer was designed by French and Church for absorption measurements on biological materials.[9] Since then, several wavelength modulation spectrometers have been built,[10-14] for study of optical properties of solids.

The main difficulty of the wavelength-modulation scheme is the elimination of the huge background in the derivative spectrum arising from differentiation of the spectral contribution of all the optical components in the system. This background can be two to four orders of magnitude larger than the sample spectrum. It is particularly serious in the UV region where arc lamps with unavoidable narrow spectral lines must be used as light sources.

A two-beam method is often used to eliminate the background. In most wavelength-modulation spectrometers, the sample spectrum is extracted from the background by subtraction of the two signals from the two beams. However, this is usually effective only when the background is not much larger than the sample spectrum. French and Church,[9] on the other hand, devised an ingenious feedback loop which is able to achieve complete compensation of the background. Unfortunately, their optical system was designed in such a way that it easily picks up spurious signals.

We have modified the design of French and Church,[9] and have succeeded in building a wavelength-modulation spectrometer free of background trouble in the tested range between 2000Å and 8000Å. This spectral range can easily be extended farther into the UV and into the infrared. For measurements of the reflectivity R, the spectrometer has a sensitivity of $\Delta R/R \lesssim 10^{-5}$. In addition, it can also yield simultaneously two signals R and $dR/Rd\lambda$, or any of the other two combinations, $(R,\ dR/d\lambda)$ and $(1/R,\ dR/Rd\lambda)$.

In the next section, we first discuss the principles of operation of our wavelength-modulation spectrometer. Then, in Section III, we give a description of the optical and electronic system. Finally, in Section IV, we present an example and discuss some features of the system.

II. PRINCIPLES OF OPERATION

A. Principles of Wavelength Modulation

Let $g(\lambda-\lambda_0)$ be the symmetric slit function of the spectrometer centered at λ_0 and normalized to $g(0) = 1$, and $I(\lambda)g(\lambda-\lambda_0)$ be the light intensity at λ reaching the photomultiplier after passing through the spectrometer. Then, the electric signal at the output is given by

$$S(\lambda_0) = \int_{-\infty}^{\infty} g(\lambda-\lambda_0)G(\lambda)I(\lambda)d\lambda \tag{1}$$

where $G(\lambda)$ is the coefficient for converting light intensity into the final output electric signal.

If the central wavelength λ_0 is modulated such that $\lambda_0 = \lambda_0^0 + A\cos\omega t$, then by expanding $T(\lambda) \equiv G(\lambda)I(\lambda)$ into a power series about λ_0^0 we have

$$S(\lambda_0^0,t) = \int_{-\infty}^{\infty} g(\lambda-\lambda_0^0-A\cos\omega t)\left[T(\lambda_0^0) + T'(\lambda_0^0)(\lambda-\lambda_0^0) + \frac{1}{2}T''(\lambda_0^0)(\lambda-\lambda_0^0)^2 + \ldots\right]d\lambda \tag{2}$$

Integration term by term of the above expression yields

$$\begin{aligned} S(\lambda_0^0,t) = {} & \left[T(\lambda_0^0)W + \frac{1}{2}T''(\lambda_0^0)(\xi_2 W^2 + \frac{1}{2}A^2)W + \ldots\right] + \\ & + \left[T'(\lambda_0^0)WA + \frac{1}{2}T'''(\lambda_0^0)WA(\xi_2 W^2 + \frac{1}{4}A^2) + \ldots\right]\cos\omega t + \\ & + \left[\ldots\right]\cos 2\omega t + \ldots \end{aligned} \tag{3}$$

where we have defined

$$\xi_\alpha W^{\alpha+1} \equiv \int_{-\infty}^{\infty} g(\lambda)\lambda^\alpha d\lambda \tag{4}$$

with $\xi_0 \equiv 1$, and $\xi_2 = 0$ for odd α's resulting from the symmetry of $g(\lambda)$.

We notice that wavelength modulation causes the signal $S(\lambda_0^o,t)$ to contain all harmonics of the modulation frequency ω. The amplitude of each harmonic is a power series which converges quickly if both A and W are small. Since the electronic system usually filters out all the higher-order harmonics, we only need to retain here the dc and the first harmonic terms. Then, Eq. (3) reduces to

$$S(\lambda_0^o,t) \cong S^{DC}(\lambda_0^o) + S^{AC}(\lambda_0^o)\cos\omega t \tag{5}$$

If A and W are small, then to first order, we have

$$S^{DC}(\lambda_0^o) \cong WT(\lambda_0^o) \tag{6}$$

$$S^{AC}(\lambda_0^o) \cong WAT'(\lambda_0^o) \tag{7}$$

The above equations show that the signal obtained after detection of the wavelength modulated beam contains a dc term $S^{DC}(\lambda_0^o)$ and an ac term of amplitude $S^{AC}(\lambda_0^o)$. Both magnitudes can be measured. The dc signal $S^{DC}(\lambda_0^o)$ is now proportional to $T(\lambda_0^o)$ like in a conventional spectrometer without modulation, and the first harmonic signal $S^{AC}(\lambda_0^o)$ is proportional to the first derivative of $T(\lambda_0^o)$ with respect to λ_0^o. It is easy to show that the approximations in Eqs. (6) and (7) are valid as long as W and A are small, compared with the characteristic width of the structure in the spectrum being measured.

B. Operating Principles of the Wavelength-Modulation Spectrometer

It is clear that $T(\lambda)$ here is the product of the spectra of all optical components in the light path, with only the slit function excluded. However, we are only interested in the sample spectrum and its derivative. In order to eliminate the unwanted background, we use a two-beam scheme in our spectrometer. The light beam from the spectrometer is split into two with identical optical paths except that one beam undergoes an extra reflection from or transmission through the sample.

Following Eqs. (6) and (7) (we drop the indices of λ for simplicity), we obtain from one beam

$$S_A^{DC}(\lambda) = WT_0(\lambda) \tag{8}$$

$$S_A^{AC}(\lambda) = WA(dT_0/d\lambda) \tag{9}$$

and from the other beam,

$$S_B^{DC}(\lambda) = WT_0(\lambda)R(\lambda) \tag{10}$$

$$S_B^{AC}(\lambda) = WA\left[d(T_0R)/d\lambda\right] = WA\left[T_0dR/d\lambda + RdT_0/d\lambda\right] \tag{11}$$

where R is the reflectivity (or transmittance) of the sample. As will be discussed later, we can devise two feedback loops to make either S_A^{DC} or S_B^{DC} constant, and either S_A^{AC} or S_B^{AC} vanish. For example, with $S_A^{DC} = C$ (constant) and $S_B^{AC} = 0$, we can have $S_B^{DC}(\lambda) = CR(\lambda)$ and $S_A^{AC} = CA(dR/Rd\lambda)$ from Eqs. (9) and (10). Other combinations enable us to measure simultaneously either R and $dR/d\lambda$, or $1/R$ and $dR/Rd\lambda$.

III. EXPERIMENTAL LAYOUT

We show in Fig. 1 a block diagram of the entire system of our wavelength-modulation spectrometer. Let us consider the optical part of the system first.

A 1/2-meter Jarrell-Ash monochromator with adjustable slits is used in the setup. To achieve wavelength modulation of light, several different methods have been proposed.[9-15] In our case, we use a vibrating mirror to perturb the optical path inside the monochromator periodically. The beam emerging from the exit slit is then wavelength-modulated. However, in order not to modify a commercial monochromator internally, we have used an external slit E to provide the function of the entrance slit with the help of the spherical mirror S_1 as shown in Fig. 1. The vibrating mirror M, mounted on a torsional tuning fork with a frequency of 1 KHz, is then inserted between E and S_1. The beam from the exit slit of the monochromator is now reflected by spherical mirror S_2 and focused on the beam chopper C which splits the beam alternatively into a transmitted beam and a reflected beam. The transmitted beam is focused on the sample by the spherical mirror S_3, and then the light reflected from the sample is, in turn, focused on the photodetector by the spherical mirror S_4. On the other hand, the reflected beam from the chopper is directly focused at the same spot on the photodetector by the spherical mirror S_3'. Here, care is taken to make the optical paths of the two beams as equivalent as possible. In particular, it is important that the two beams go through the same number of mirror reflections. All the mirrors are MgF_2-coated Al mirrors for efficient reflection in the UV.

Another important component in the optical system is a saw-tooth diaphragm D located in front of the monochromator on the entrance side. Its position in the beam affects the spectral function $I(\lambda)$ in Eq. (1). If the diaphragm is now driven via a motor by the electrical signal S_A^{AC} (or S_B^{AC}), then it will automatically position itself so as to make S_A^{AC} (or S_B^{AC}) vanish. This feedback system is important for the elimination of the large background in the derivative spectrum as we mentioned earlier.

Next, we consider the associated electronic system in the setup with the block diagram of Fig. 1. As we mentioned earlier, the beam chopper, acting as an optical switch at a frequency of 5Hz, splits the light beam into two beams which then hit the photodetector alternatively. The output from the photodetector appears as a 5 Hz square wave with 1 KHz sinusoidal modulation superimposed on it (Fig. 2). The two portions of the square wave can be described by $s_A^{DC} + s_A^{AC} \cos\omega t$ and $s_B^{DC} + s_B^{AC} \cos\omega t$, respectively.

The preamplifier following the photodetector adds a constant negative voltage $-V_c$ to the square wave. Then, and electronic switch operating synchronously with the optical switching alternatively sends the signals from the two beams into two channels. At the input of each channel, a capacitor in parallel is used to keep the dc level unchanged during the off period.

The dc and the ac signals in each channel now go into a dc amplifier and a lock-in amplifier respectively. From the two channels, we then have altogether four output signals, $S_A^{DC} - C$ and $S_B^{DC} - C$ from the dc amplifiers and S_A^{AC} and S_B^{AC} from the lock-in amplifiers. We use either

$S_A^{DC} - C$ or $S_B^{DC} - C$ as an error signal in a negative feedback loop to control the gain of the photodetector. Consequently, we have either $S_A^{DC} = C$ or $S_B^{DC} = C$. We also use either S_A^{AC} or S_B^{AC} as the error signal to drive the diaphragm as we discussed earlier. This gives us either $S_A^{AC} = 0$ or $S_B^{AC} = 0$. Finally, two of the output signals not involved in the feedback are recorded either on chart recorders or on digital units.

One of the important parts in this two-beam system is the switching unit. We realize that during switching, the light spot hits the edge of the chopper blade, and consequently, part of the light beam is transmitted and part of it reflected. If this period of actual switching operation were not blanked, a false signal would appear at the output. This short blanking interval for both channels is provided in our system by a second electronic switch in the switching unit.

IV. DISCUSSION AND EXAMPLES

The wavelength-modulation spectrometer described in the previous sections has been used to generate excellent derivative spectra of many semiconductors[16] and metals.[17] Several important aspects of the spectrometer are worth emphasizing here.

1. With the modulation scheme we choose and the optical arrangement we use, the positions of the light spot on the sample and on the photodetector remain stationary. This avoids error which would be induced by the motion of the light spot on the sample and on the photodetector as a result of the slightly different local response of an optical surface. Such a difficulty exists in the system of French and Church.[9]

2. By making the optical paths of the two beams in the system more or less equivalent, we have minimized the error which might be induced otherwise. In particular, we focus the two beams at the same spot on the photodetector. Focusing of the two beams at different spots on the photodetector or the use of two photodetectors is often the source of trouble in some wavelength-modulation spectrometers.[10-13]

3. We use feedback instead of electronic subtraction in our system to cancel the huge background in the derivative spectrum. This scheme is obviously more effective whenever the background is comparable with or larger than the signal.

The derivative spectra we have obtained with this system are essentially free of background trouble. With good optical alignment, zeroes in the derivative spectrum match well with the maxima and minima in the conventional spectrum. As an example, we show in Fig. 3 the recorded spectra of $dR/d\lambda$ and R of GaAs at liquid He temperature between 2000Å and 4500Å. The cancellation of background in this spectral range is always more difficult since a Xe arc lamp is used as the light source. Without cancellation, the sharp Xe spectral lines would appear in the derivative spectrum as a background three orders of magnitude larger than the signal we try to detect. As seen in Fig. 3a, our derivative spectrum of GaAs shows almost complete cancellation of the background. Arrows in the figure point at the small residual structures of the Xe lines which are still present, but well within the tolerable limit. This spectrum was taken with a slit width of 15Å, a peak-to-peak modulation amplitude of 30Å, a scan rate of 50Å/min, and a lock-in time constant of 10 sec. Some tests with smaller slit width and modulation amplitude were performed to insure that there was no distortion of the narrowest peaks.

As seen from Eq. (7), for better signal-to-noise ratio, the modulation amplitude A and the slit width W should be as large as possible, but then for better resolution, they should be as small as possible. Normally, we choose A and W to be sufficiently small compared to the width of the narrowest peaks to be observed, and in order to maximize the signal, we shoose A and W to be equal.

To minimize noise, we should keep the time constant of the lock-in detector for the signal as large as possible, but compatible with the scanning rate of the spectrometer. However, it is interesting to remark that a slower scanning rate plus a larger lock-in time constant would not make cancellation of the Xe lines in Fig. 3a better. There, the small residual structures actually came in because the Xe lines were narrower than the modulation amplitude so that the approximations in Eqs. (6) and (7) became less perfect and, hence, complete cancellation of the Xe lines was not possible.

To show the consistency of the derivative spectrum with the conventional spectrum, we obtain $R(\lambda)$ in Fig. 3c by numerically integrating $dR/d\lambda$ of Fig. 3a, and compare it with the measured $R(\lambda)$ in Fig. 3b. It is seen that the two spectra in Fig. 3b and 3c agree very well.

In principle, the derivative spectrum can be obtained from the conventional spectrum by simple numerical differentiation.[18] However, we have found that only with a sophisticated averaging program in the numerical calculation can we achieve as good a signal-to-noise ratio in the derivative spectrum as we can obtain directly from our spectrometer. Incidentally, the advantage of derivative spectroscopy is clearly manifested in Fig. 3 since it would be difficult to recognize the small structure in R without the help of the derivative spectrum $dR/d\lambda$.

We have shown how to build a wavelength modulation spectrometer to measure simultaneously (R or $1/R$) and ($dR/d\lambda$ or $dR/Rd\lambda$) over a wide spectral range, using mostly commercially-available components. The spectrometer can be used to study optical properties of materials by either absorption or reflection measurements with or without external perturbation. Although the present operating range of our spectrometer is between 2000Å and 8000Å, extension further into the infrared and the UV regions needs only slight modification. We are presently in the process of extending the UV operating range to about 1400Å. Modification of the spectrometer to yield second derivative spectra is also possible.

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REFERENCES

*This paper is a condensation of a portion of the PhD thesis (1971) by Ricardo Zucca, University of California at Berkeley (unpublished).

†Present address: North American Rockwell Science Center, Thousand Oaks, California 91360.

‡On leave at Harvard University.

1. See, for example: G. E. Pake, Nuclear Magnetic Resonance, Solid State Physics, edited by F. Seitz, D. Turnbull and H. Ehrenreich, (Academic Press, New York, 1956), v. 2, p. 1; C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, (McGraw-Hill, New York, 1955).

2. G. Bonfiglioli and P. Brovetto, Appl. Opt. 3, 1417 (1964).

3. J. C. Phillips, The Fundamental Optical Spectra of Solids, Solid State Physics, edited by F. Seitz, D. Turnbull and H. Ehrenreich, (Academic Press, New York, 1966), v. 18, p. 55.

4. See, for example: Modulation Spectroscopy, M. Cardona (Academic Press, New York, 1969).

5. B. O. Seraphin and N. Bottka, Phys. Rev. 145, 628 (1966); M. Cardona, K. L. Shaklee and F. H. Pollak, Phys. Rev. 154, 696 (1967).

6. G. W. Gobeli and E. O. Kane, Phys. Rev. Letters 15, 142 (1965); W. E. Engeler, W. Fritzsche, M. Garfinkel, and J. J. Tiemann, Phys. Rev. Letters 14, 1605 (1965); M. Garfinkel, J. J. Tiemann, and W. E. Engeler, Phys. Rev. 148, 659 (1968).

7. B. Batz, Solid State Comm. 4, 241 (1966); E. Matatagui, S. G. Thompson, and M. Cardona, Phys. Rev. 176, 950 (1968).

8. E. Y. Wang, W. A. Albers and C. E. Bleil, II-VI Semiconducting Compounds, 1967 Conference, edited by D. G. Thomas, (Benjamin, Inc., New York, 1967), p. 136.

9. C. S. French and A. B. Church, Annual Report of Carnegie Institute of Washington, p. 162 (1954-55).

10. I. Balslev, Phys. Rev. 143, 676 (1966).

11. G. Bonfiglioli, P. Brovetto, G. Busca, S. Levialdi, G. Palmieri, and E. Wanke, Appl. Opt. 6, 447 (1967).

12. K. L. Shaklee and J. E. Rowe, Appl. Opt. 9, 627 (1970).

13. Ricardo Zucca, PhD Thesis, University of California at Berkeley, 1971 (unpublished).

14. M. Welkowsky and R. Braunstein, Rev. Sci. Instr. 43, 399 (1972).

15. K. G. McWilliam, J. Sci. Instr. 36, 51 (1959).

16. R. Zucca and Y. R. Shen, Phys. Rev. B1, 2668 (1970); C. V. de Alvarez, J. P. Walter, M. L. Cohen, J. Stokes, and Y. R. Shen, Phys. Rev. B6, 1412 (1972).

17. C. Y. Fong, M. L. Cohen, R. Zucca, J. Stokes, and Y. R. Shen, Phys. Rev. Letters 25, 1486 (1970); J. Stokes, Y. R. Shen, Y. W. Tsang, M. L. Cohen, and C. Y. Fong, Phys. Letters 38A, 347 (1972).

18. D. D. Sell and E. O. Kane, Phys. Rev. B5, 419 (1972);
S. E. Stokowski and D. D. Sell, Phys. Rev. B5, 1636 (1972).

19. J. Koo, Y. R. Shen, and R. R. L. Zucca, Sol. State Comm. 9, 2229 (1971).

FIGURE CAPTIONS

Fig. 1 Block diagram of the wavelength-modulation spectrometer. E, external slit; M, vibrating mirror; D, sawtooth diaphragm; C, beam chopper; S_1, S_2, S_3, S_3', S_4, spherical mirrors.

Fig. 2 Output waveform from the photodetector.

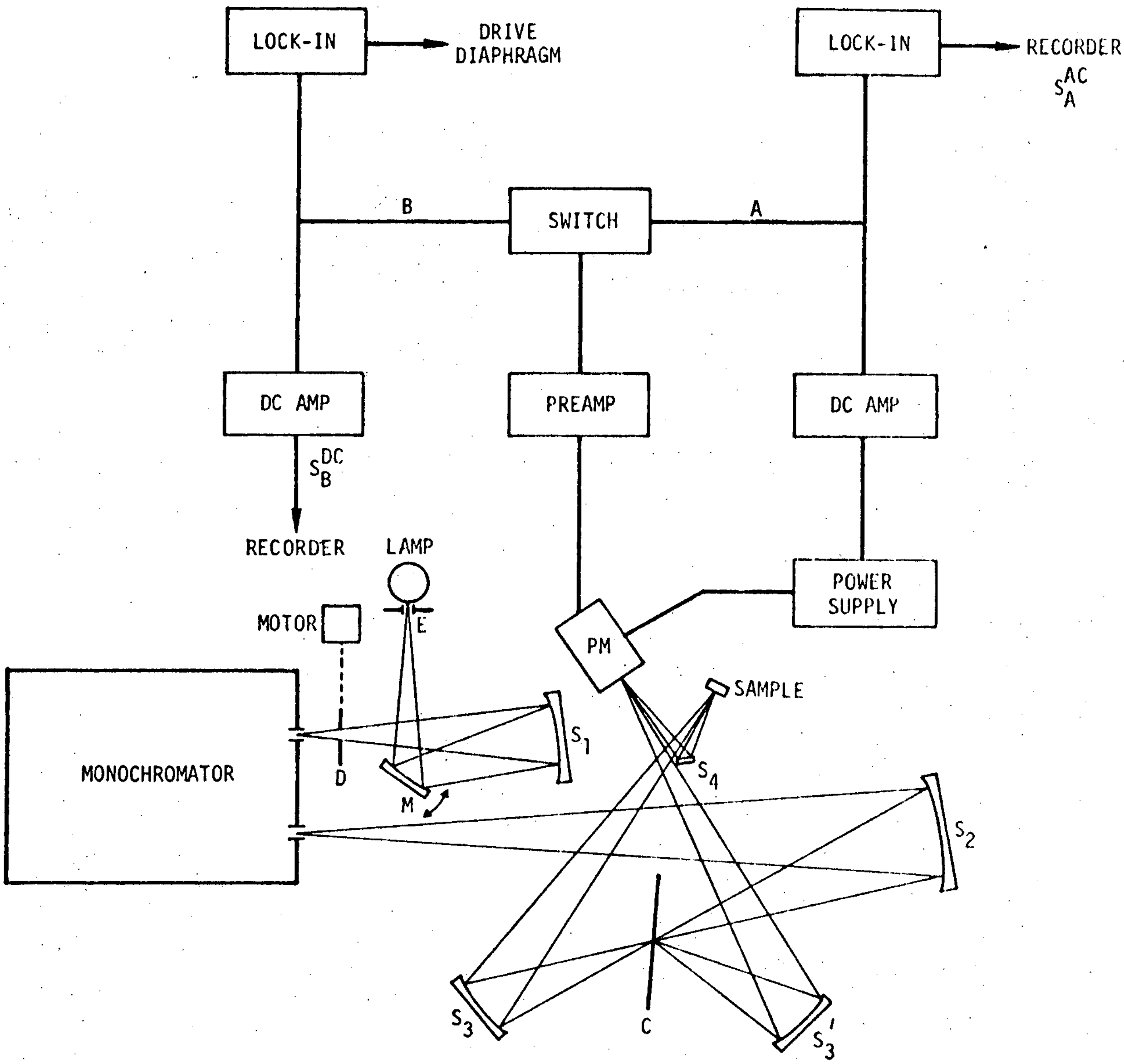
Fig. 3 GaAs spectra at liquid He temperature.

(a) Derivative spectrum $dR/d\lambda$ versus λ

(b) Conventional spectrum R versus λ

(c) R versus λ obtained by numerical integration of $dR/d\lambda$ in (a)

Arrows in (a) point at the residual structures of the Xe lines.



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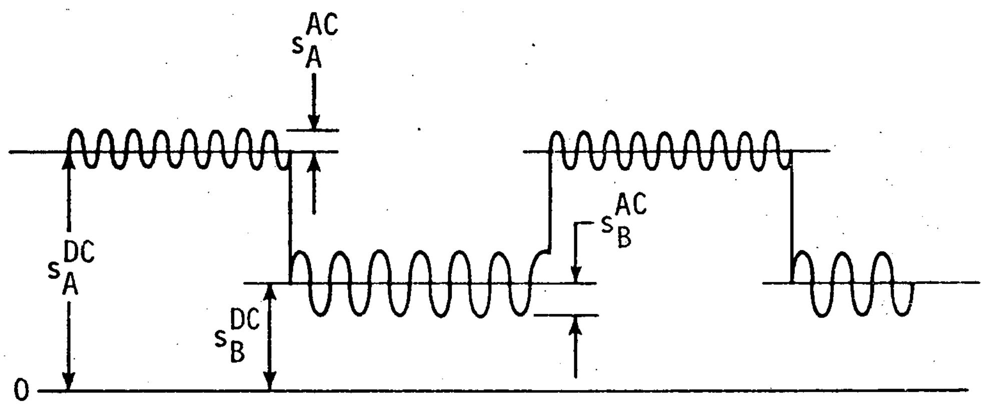

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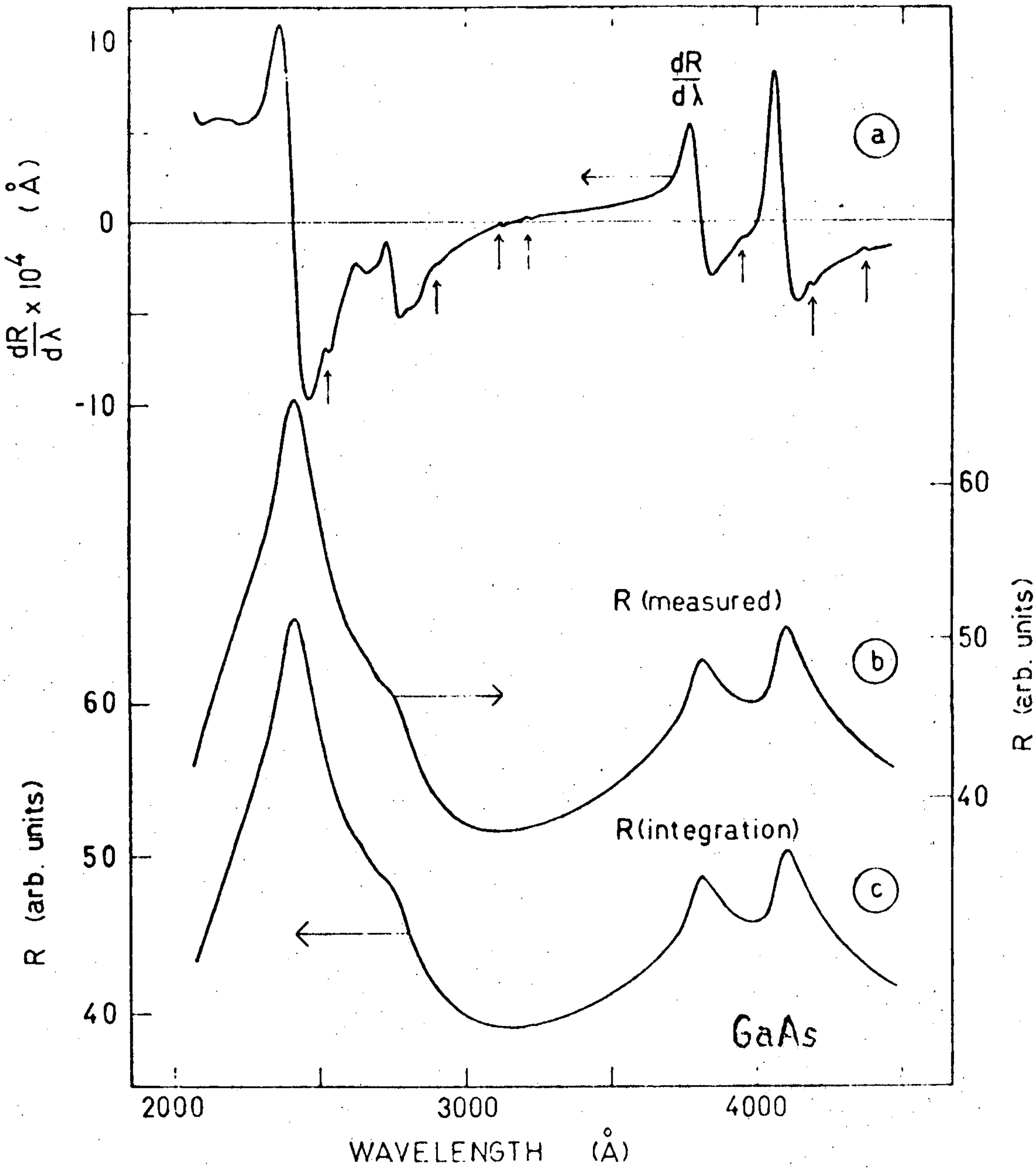
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2000
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4000
WAVELENGTH (Å)

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